

## Polarography of N-Phenylthiourea & Related Compounds

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Received 28 June 1976; revised 9 November 1976; accepted 23 December 1976

N-Phenylthiourea and its various other derivatives have been polarographically studied in aq. 0.1M NaOH as well as in 0.1M NaOH in 10% aq. DMF solutions. Waves are found to be reversible with the electrode reaction involving two electrons. Effect of substituents in the phenyl group on the half-wave potentials has been investigated according to Hammett equation and reaction constants, 0.12 V and 0.18 V have been calculated in aqueous and 10% aq. DMF media, respectively. Effect of addition of DMF has been found to alter the radii of solvated entities (polarographically active), thereby increasing the values of diffusion currents significantly in 10% DMF at the same concentrations of thioureas as studied in aqueous solutions.

**T**HIUREA and its derivatives have been commercially employed as surface protective agents<sup>1</sup>, and as chemicals for the preservation of dyes<sup>2</sup>. They have also found important uses in biochemistry and in inorganic chemistry due to their remarkable coordinating power with various metals<sup>3,4</sup>. Polarography is extensively being used in all the above mentioned fields and many others.

Before applying polarography as a tool in establishing degree of preservation of various alkyl and aryl substituted as well as thiourea itself, for various dyes, it was thought worthwhile to study detailed polarographic behaviour of hitherto unstudied some N-phenylthiourea derivatives.

Thiourea<sup>5</sup>, some alkylthioureas, phenyl-, and diphenyl-thioureas have been polarographically studied<sup>6</sup>. However the studies so far made provide insufficient data. In the present investigation, N-phenylthiourea and its derivatives have been subjected to polarographic study in aqueous as well as aquo-10% dimethylformamide media. The effect of various substituents in the benzene ring attached to thiourea has been systematized on the basis of Hammett equation<sup>7</sup>.

### Materials and Methods

Sodium hydroxide, sodium acetate and borax were all BDH (AR) products. DMF was a Riedel (Germany) product.

N-Phenyl and other substituted thioureas were prepared in the laboratory by the action of ammonium thiocyanate on hydrochlorides of corresponding amines<sup>8,9</sup>. The crystallization and purification of different compounds needed special treatments since most of them got decomposed during recrystallization. The following conditions were maintained for getting pure products.

Warm (on water-bath) 25% ethanolic solution of N-phenylthiourea when cooled to room temperature gave crystals of pure phenylthiourea which were filtered and dried by slow evaporation.

Ethanolic solution (20%) of *o*-tolylthiourea was stirred constantly on a water-bath till boiling and

then cooled in an ice-bath and dried by slow evaporation.

Hot 25% ethanolic solution of *m*-tolylthiourea was gradually cooled and kept in an ice-bath for 30 min with constant stirring, filtered and dried.

Ethanolic solutions (30%) of *p*- and *m*-chlorophenylthioureas were boiled on a water-bath and cooled vigorously under tap water, filtered and dried.

*p*-Anisoylthiourea was recrystallized from 25% hot ethanol, ice-cooled with continuous stirring, filtered and dried by slow evaporation.

Ethanolic solution (40%) of *m*-anisoylthiourea was boiled for 15 min on a water-bath then vigorously cooled first under tap-water then in ice-bath; crystals thus obtained were filtered and dried slowly.

Ethanolic solutions (25%) of *o*- and *p*-phenytoylthioureas were boiled and vigorously cooled under tap-water to give crystals which were then filtered and dried slowly.

*m*-Phentoylthiourea was dissolved in 25% methanol and cooled in ice-bath with stirring, filtered and dried.

The solutions were prepared in doubly distilled water. Triply distilled mercury was used for d.m.e. and test solutions were de-oxygenated for about 15-20 min.

Manually operated 'Toshniwal' polarograph with capillary characteristics  $2.487 \text{ mg}^{2/3} \text{ sec}^{-1/2}$  with scalamp (Pye) galvanometer, for current recordings was used. Saturated calomel electrode served as the reference electrode.

For coulometric (controlled potential electrolysis) analysis a manual assembly was adjusted. Electrolysis of  $1.0 \times 10^{-4} \text{ M}$  N-phenylthiourea in 0.1M NaOH was performed using a large mercury pool anode in a cell recommended by Lingane<sup>10</sup> with internal auxiliary electrode and saturated calomel electrode as reference electrode. The solution was electrolysed for about 4 hr at  $-0.6 \text{ V}$  under nitrogen atmosphere.

Polarograms of all the thioureas at various concentrations and at various heights of mercury

column in 0.1M NaOH aqueous and 10% aq. DMF solutions were recorded.

## Results and Discussion

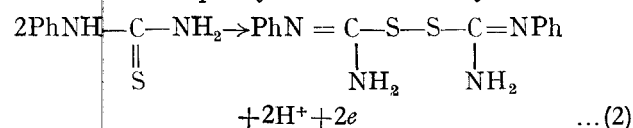
In alkaline medium the thioureas employed give only one (in the concentration range studied — up to  $4 \times 10^{-4}M$ ) well-defined diffusion controlled ( $i_d \propto C$  and  $i_d \propto \sqrt{h}$ ) anodic waves. It was quite interesting to observe that half-wave potentials of the waves at various concentrations remained practically constant. This may be taken as an approximate criterion of reversibility. Temperature coefficients for N-phenylthiourea by Nejedly<sup>11</sup> method in the range 30°–60° was calculated to be 1.61% confirming a diffusion-controlled electrode process.

Linear plots were obtained when Eq. (1) of the reversible anodic wave was applied, i.e.

$$E_{d.e.} = E_{1/2} - \frac{0.059}{n} \ln \frac{i_d - i}{i} \quad \dots(1)$$

The value of slope 29.6 mV gives the value of  $n = 1.99$  indicating that two electrons are involved in the electrode process. Log plots of other thioureas are similar to that of phenylthiourea.

Like thiourea<sup>5</sup> the mechanism of anodic electrode process, in the case of phenylthioureas may also involve mercury salt formation as suggested earlier by Zuman and coworkers<sup>6</sup>, Liberty<sup>12</sup> and Sartori and Calzolani<sup>13</sup> but not an anodic oxidation of the compounds. Taking N-phenylthiourea as a typical case and if the electrode process be considered an oxidation of N-phenylthiourea, we may write



The potential at every point on the wave will be given by Eq. (3)

$$E_{d.e.} = \text{constant} - \frac{RT}{nF} \ln \left( \frac{[\text{PhNH}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{NH}_2]_0^2}{[\text{PhN}=\underset{\text{NH}_2}{\underset{\parallel}{\text{C}}}-\text{S}-\underset{\text{NH}_2}{\underset{\parallel}{\text{C}}}=\text{NPh}]_0} \right) \quad \dots(3)$$

The subscript '0' denotes concentration of N-phenylthiourea and its oxidized product at the surface of the mercury drop. Equation (3) in terms of current, ignoring activity coefficients and diffusion coefficients of the reduced and oxidized forms, and putting  $n=2$ , may be written as,

$$E_{d.e.} = \text{constant} - \frac{0.059}{2} \ln \left[ \frac{(i_d - i)^2}{i} \right] \quad \dots(4)$$

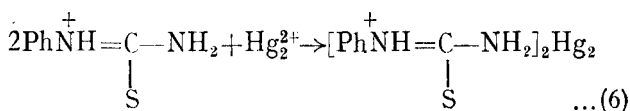
The other mechanism based on soluble salt or complex formation with mercury at d.m.e. can be represented as follows

Since mercurous ions are released by the anodic oxidation of mercury from the d.m.e. as shown in Eq. (5),



Considering the N-phenylthiourea in Zwitterion form<sup>17</sup> the complex formation takes place in

accordance with Eq. (6)



So for the combined anodic process according to Eqs. (5) and (6) the potential at every point on the wave will be given by Eq. (7)

$$E_{d.e.} = E_{1/2} - \frac{0.059}{n} \ln \left( \frac{[\text{Hg}_2^{2+}]}{[\text{PhNH}=\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{NH}_2]_2\text{Hg}_2} \right) \quad \dots(7)$$

Since ( $\text{Hg}_2^{2+}$ ) is electroactive species and is present in great excess, the electrode process would only have the ( $\text{Hg}_2^{2+}$ ) equivalent to the concentration of

$\text{PhNH}=\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$  ions diffusing towards the electrode. Again ignoring the activities and activity coefficients of the electroactive species, Eq. (7) in terms of current will be

$$E_{d.e.} = E_{1/2} - \frac{0.059}{n} \ln \left( \frac{(i_d - i)}{i} \right) \quad \dots(8)$$

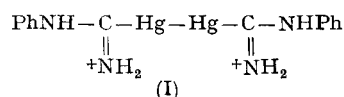
Now according to Eqs. (4) and (8) plots of  $E_{d.e.}$  versus  $\log \left[ \frac{(i_d - i)^2}{i} \right]$  or  $E_{d.e.}$  versus  $\log \left( \frac{i_d - i}{i} \right)$  should

be linear. When the respective plots were drawn, it was found that while the plot  $E_{d.e.}$  versus  $\log \left( \frac{i_d - i}{i} \right)$  is a linear (Fig. 1a), the plot of  $E_{d.e.}$  versus

$\log \left[ \frac{(i_d - i)^2}{i} \right]$  is not linear (Fig. 1b) establishing that

Eq. (8) is applicable to the anodic electrode process.

To confirm the electrode process and its reversibility, polarogram of  $1.0 \times 10^{-4}M$  freshly electrolysed N-phenylthiourea solution in 0.1M NaOH was recorded (Fig. 2a). It gave a cathodic wave with  $E_{1/2} = -0.474$  V and slope of the log plots equal to 0.0289 V, due to the reduction of the soluble mercury complex to mercury, thereby confirming a reversible process. Aged electrolysed solution gave a composite wave with almost same  $E_{1/2}$  as that given by N-phenylthiourea (Fig. 2b). Thus the compound formed is of a type similar to that reported by Edsberg<sup>5</sup> for thiourea. The compound formed with phenylthiourea can be represented by structure (I).



Half-wave potentials of N-phenylthiourea and its derivatives presented an interesting study in alkaline aqueous and alkaline aq. 10% DMF. The anodic reaction of thiourea is facilitated due to the existence of Zwitterions. The Zwitterion formation is mainly governed by (a) the effect of various substituents in the phenyl ring and consequent electromeric

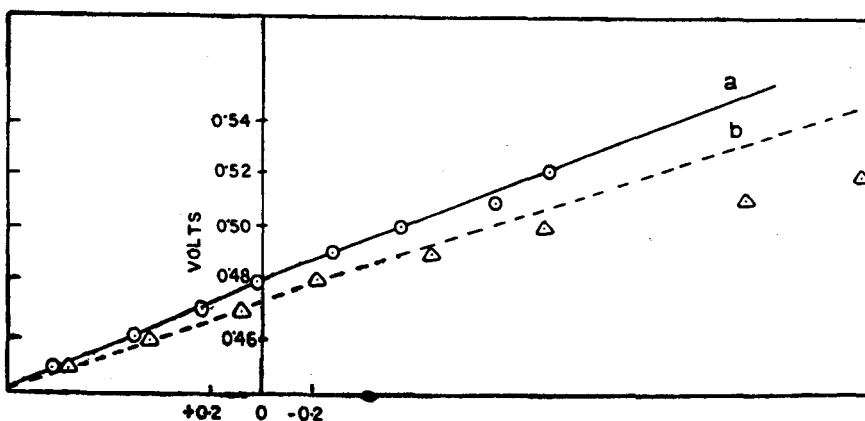


Fig. 1 — Log plot of N-phenylthiourea [(a)  $-E_{d.e.}$  versus  $i_d - i/i$ ; (b)  $-E_{d.e.}$  versus  $(i_d - i)^2/i$ ]

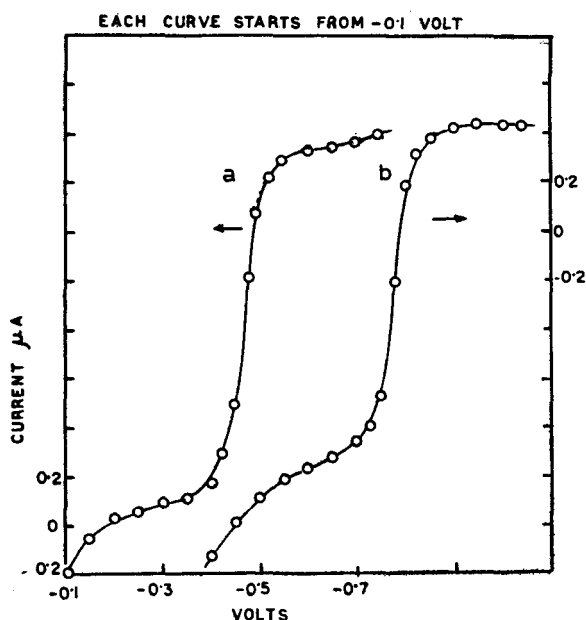


Fig. 2 — Current-voltage curve of (a) freshly electrolysed and (b) aged electrolysed N-phenylthiourea in 0.1M NaOH (aq.)

changes at the reaction site and (b) viscosity and dielectric constant of the solvent.

Symmetrical thiourea with  $E_{1/2} = -0.32$  (aq.),  $-0.14$  V (10% DMF) with respect to 0.1M NaOH exhibits greatest tendency of Zwitterion formation due to high resonance energy. Presence of benzene ring at one of the nitrogen atoms of thiourea disrupts the symmetry and decreases resonance energy causing a  $-I$  (negative inductive effect) on nitrogen of thiourea and displacement of electron towards phenyl ring makes Zwitterion formation comparatively difficult, hence more  $-ve$  value of  $E_{1/2}$  (Table 1).

The  $-I$  effect of phenyl ring would further be influenced by the contributions of the polar ( $P$ ), steric ( $S$ ) and resonance ( $M$ ) effects of various substituents. According to Zuman<sup>15</sup> the shift of the half-wave potentials relative to that of parent compound is due to the additive effects of  $P$ ,  $S$  and  $M$ , i.e.  $\Delta E_{1/2} = P + S + M$ . Modified Hammett equation<sup>7</sup> (Eq. 9) is the most generally used form of the above expression

$$\Delta E_{1/2} = \rho \pi R \sigma x \quad \dots (9)$$

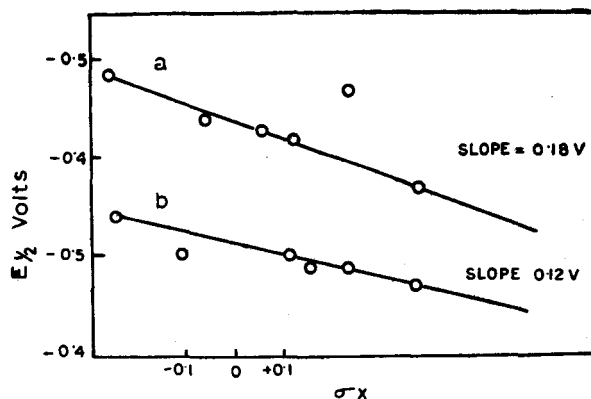


Fig. 3 — Plots of  $E_{1/2}$  of various thioureas versus Hammett total polar substituent constants ( $\sigma x$ ) in (a) aq. 10% DMF and (b) aqueous medium

Eq. (9) is used for benzenoid compounds bearing a polarographically active group  $R$  in the side chain and a substituent ' $X$ ' in the  $m$ - or  $p$ -position.  $\rho \pi R$  is the reaction constant, expressed in volts, characterizing the reducible group  $R$ . It depends on the reaction conditions, i.e. supporting electrolyte, solvent etc.  $\sigma x$  values are Hammett total polar substituent constants<sup>7</sup>, depending only on the type and position of substituents.

$E_{1/2}$  values of various thioureas were plotted, against  $\sigma x$  values (Fig. 3). From the slopes the values of reaction constants obtained are:

For aq. soln = 0.12 V

For aq. 10% DMF soln = 0.18 V

According to Hammett, positive values of reaction constants show a nucleophilic effect on reaction site which is more in 10% DMF solutions hence  $E_{1/2}$  values are 20-120 mV more positive in 10% DMF than in aqueous solution (Table 1). Viscosity and dielectric constant seem to have little or no effect owing to low percentage of DMF<sup>16</sup> as compared to water. Possibly DMF molecules from 10% solutions penetrate the primary solvation sheath around the diffusing thiourea molecules facilitating Zwitterion formation and lowering the ion dipole interaction energy at the d.m.e. and hence more  $+ve$   $E_{1/2}$  values. The effect is much less in the case of chlorophenyl derivatives, probably due to much

TABLE 1 — HALF-WAVE POTENTIAL AND CURRENT CONSTANTS OF VARIOUS THIOUREAS

No.	Thiourea	Aq. 0.1M NaOH			0.1M NaOH in aq. 10% DMF		
		$E_{1/2}$ (V)	$-i_d$ ( $\mu$ amp)	$I^*$	$E_{1/2}$ (V)	$-i_d$ ( $\mu$ amp)	$I^*$
1	Thiourea	-0.32	1.48	5.97	0.14	2.23	9.04
2	N-Ph.	-0.479	1.42	5.77	-0.31	2.24	9.12
3	<i>m</i> -Tolyl	-0.50	1.25	5.04	-0.39	2.04	8.23
4	<i>o</i> -Tolyl	-0.485	1.10	4.43	-0.31	1.89	7.62
5	<i>p</i> -Anisoyl	Insoluble	—	—	-0.42	2.22	9.04
6	<i>m</i> -Anisoyl	-0.488	1.28	5.12	-0.42	1.97	7.94
7	<i>p</i> -Chlorophen.	-0.49	1.26	5.08	-0.47	2.22	9.04
8	<i>m</i> -Chlorophen.	-0.47	1.31	5.28	-0.37	2.25	9.17
9	<i>o</i> -Phentoyl	Insoluble	—	—	-0.32	1.74	7.01
10	<i>p</i> -Phentoyl	do	—	—	-0.34	2.02	8.14
11	<i>m</i> -Phentoyl	do	—	—	-0.43	2.23	9.09

$$*I = i_d/cm^2/3t^{1/6}$$

stronger polar effect on reaction site, through the ring.

Higher values of  $i_d$  or  $I$ , the current constant, in 10% DMF as compared to aqueous solutions (Table 1) may be explained as follows: The addition of DMF in water alterst he radii of solvated entities to a significant extent thereby affecting values of diffusion coefficients of thioureas, as a result higher values of diffusion currents are obtained. Similar explanation was put forward by Hale and Parsons<sup>16</sup> while studying various solvent mixtures.

#### Acknowledgement

The author gratefully thanks Dr D. Sen, Head of the Department of Chemistry, for his kind cooperation and encouragement.

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